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POLARIZATION PROCESSES IN ELECTROTECHNICAL PORCELAIN WITHIN A WIDE FREQUENCY RANGE

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The composition and microstructure of ultraporcelain UF-46 and electroporcelain M-23 are considered. Their main physicochemical properties needed to produce some types of insulators intended for operation in a wide temperature interval are described. Special attention is paid to the dielectric properties of electrotechnical porcelain; methods for improving these properties are discussed.

Depending on the purpose and requirements imposed, ceramic materials and products should have prescribed electromechanical, thermophysical, and special properties. Electroc ceramic materials are used to produce certain types of insulators that have to operate in a wide temperature interval [1, 2].

An advantage of electric porcelain over other insulating ceramic materials is the fact that it enables one to make large-size high-voltage insulators of a complex configuration.

Electroporcelain can be classified as follows based on its purpose and properties: normal high-voltage porcelain used in the production of high-voltage line and apparatus insulators; high-voltage porcelain with an increased quartz content used to make high-voltage apparatus insulators with improved electromechanical properties; high-voltage alumina porcelain for high-voltage apparatus insulators with elevated mechanical strength; low-voltage porcelain used in the production of insulators and insulating parts for plants up to 500 V generating direct and alternating current and weak current plants; zircon and ascharite porcelain intended for making insulators with increased thermal-shock resistance [3].

Three types of compositions are currently used for electrotechnical porcelain: the standard feldspar composition containing 45 – 50% argillaceous materials, 20 – 25% quartz, and 25 – 30% feldspar; the quartz composition containing 27 – 31% quartz, 45 – 50% argillaceous materials, and 17 – 22% feldspar; and the alumina composition with an increased content of alumina due to a decreased quartz content.

The most important dielectric characteristic of porcelain is electric breakdown strength which mainly depends on the quantity of the vitreous phase. A high content of a high-melt-

ing vitreous phase makes porcelain different from other ceramic materials.

The electric breakdown of an insulator is preceded by the increased conductivity of porcelain under the effect of an electric field related to an accompanying temperature rise. The conductance of feldspar porcelain is ionic and is usually determined by the content of sodium and potassium in the vitreous phase.

The variation in volume resistivity of porcelain depending on temperature (up to 400°C) proceeds exponentially regardless of the $K_2O : Na_2O$ ratio.

The electric strength of porcelain depends on the duration of the stress effect. This is due to ionization processes. The electric strength of porcelain at a normal temperature has a weak correlation with the $K_2O : Na_2O$ ratio in the vitreous phase. However, this ratio has a significant effect on the temperature at which a perceptible decrease in breakdown voltage is registered. A decrease in the $K_2O : Na_2O$ ratio in porcelain lowers the temperature and initiates a thermal breakdown. The drop in breakdown voltage under heating is due to the sharp increase in dielectric loss. The presence of calcium in feldspar has a positive effect on the electric and mechanical strength of porcelain.

The service strength of porcelain also depends on stresses developed in the vitreous phase at the temperature of transformation from a viscoplastic state to an elastic state (900 – 750°C). The structure of the vitreous phase in porcelain changes with time under the effect of mechanical and thermal factors and the electric field [4].

Alumina introduced in a porcelain mixture substantially increases the strength of the insulator. The quantity and structure of mullite has a substantial effect on strength; an insufficient quantity decreases strength.

The thermal strength of a product to a large extent depends on such characteristics as the degree of homogeneity

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of the material structure, the composition of the vitreous phase, the quantity of mullite, the shape and size of the product, etc.

Samples of electric porcelain subjected to the long-term effect of a constant electric field at 100–300°C exhibit substantial deterioration of their electric and mechanical properties.

It is possible to obtain porcelain with good dielectric parameters by introducing specially synthesized crystallizing glasses into a ceramic mixture instead of the quartz and feldspar components. The dielectric loss tangent and dielectric permeability of samples increase with increasing temperature [4].

The electron part of polarization in an ionic crystal decreases with increasing temperature due to decreasing density of the material, and the ionic part of polarization is affected by two opposite factors: decreasing density and weakening of elastic bonds, which cause a decrease in the elastic bond coefficient. The dielectric permeability of ionic cubic crystals with increasing temperature grows relatively little and is nearly linearly.

Using the known relationship for complex dielectric permeability ε and refractive index $n = \sqrt{\varepsilon}$ formally applicable within a wide range of frequencies and for all classes of materials (conductors, semiconductors, dielectrics), it is possible to find methods for engineering analysis of the relationships between macro- and microproperties of the material using a correlation of dielectric permeability with polarization of atoms, ions, and molecules [5].

Ultraporcelain UF-46 contains up to 35–39% vitreous phase. Its microstructure is very dense, close-grained, and consists of isometric corundum grains of size 2–3 μm , less frequently up to 10 μm . Corundum crystals are cemented by thin interlayers of mullitized glass. Pores exist in the form of very fine inclusions (1–2 μm).

Electrotechnical porcelain M-23 is one of the most common industrially used ceramic materials for making insulators, high-voltage equipment, etc. Analysis of diffraction patterns of this porcelain reveals its heterogeneous structure: its bulk consists of mullite with a high quantity of crystalline $\alpha\text{-Al}_2\text{O}_3$ and quartz cemented by an aluminosilicate vitreous phase [6].

Table 1 shows the chemical composition of ceramic samples considered.

Possible values of ε_∞ in the frequency range in which relaxation types of polarization have no effect on dielectric permeability can be estimated based on the formula [7]

$$\varepsilon_\infty = 1 + \frac{\sum n_i \alpha_i}{\varepsilon_0},$$

where n_i is the concentration of ions and α_i is the electron polarizability.

Calculations carried out for porcelain using this formula (Table 2) compared to experimental values of dielectric per-

TABLE 1

Porcelain	Mass content %							
	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	BaO	CaO	MgO	Na ₂ O	K ₂ O
UF-46	76.32	15.40	0.30	3.16	1.80	1.88	0.42	0.42
M-23	25.70	68.30	0.25	—	0.22	0.22	1.80	3.50

meability at frequency 1 MHz and in the visible spectrum range give similar results.

Taking into account the normal dispersion in the visible spectrum range produces complete coincidence of calculated values with experimental data obtained by the petrography method. Exaggerated values at frequency 1 MHz are due to the need to take into account the contribution of elastic ionic polarization in the infrared spectrum and relaxation polarization in the technical frequency range to dielectric permeability.

To calculate dielectric permeability in the IR spectrum, one should take into account the polarization contribution of stretching vibrations Al–O and Si–O in electric porcelain UF-46 and M-23. The maximum contribution to elastic electronic polarization is made by the oxygen ion, which has maximum concentration and polarizability.

Absorption bands at 600, 640, and 780 cm^{-1} in the spectrum of initial ultraporcelain are typical of corundum and can be attributed to stretching vibrations Al–O in the octahedron AlO_6 . Absorption bands at 1000, 1070, and 1155 cm^{-1} in the absorption spectrum indicate the presence of quartz in ultraporcelain UF-46.

In electroporcelain M-23 absorption bands at 780, 798, 1010, 1040, 1080, 1125, and 1175 cm^{-1} are attributed to stretching vibrations Si–O–Si. The presence of bands at 560, 660, and 725 cm^{-1} in the IR absorption spectrum of porcelain M-23 indicates the presence of the crystalline phase $\alpha\text{-Al}_2\text{O}_3$ [8].

Polarization of elastic ionic shift is typical of ionic crystals and consist in the shifting of positive ions with respect to negative ions in the crystal lattice under the effect of an electric field. Polarizability in this case is determined by the expression

$$\alpha_n = \frac{(2q)^2}{k},$$

where q is the ion charge ($q = e = 1.6 \times 10^{-19}$ Cl) and k is the elastic bond coefficient.

TABLE 2

Porcelain	Estimated values ε_∞	Experimental values ε_∞	
		at frequency 1 MHz	in visible spectrum ($\varepsilon = n^2$)
UF-46	2.9371	8.0–8.2	2.832
M-23	2.5386	6.5–7.0	2.335

TABLE 3

Porcelain	ε_{exp} in visible range	$\varepsilon(\text{Al}_2\text{O}_3)$	$\varepsilon(\text{SiO}_2)$	ε_{∞}
UF-46	2.832	1.930	0.474	5.236
M-23	2.335	3.690	0.121	6.146

Calculation of the elastic bond coefficient based on the formula proposed is difficult even for a two-atom model.

To determine this coefficient according to G. I. Skanavi [9], one can use the following formulas:

$$k = \frac{4\pi^2 c^2 m_1 m_2}{\lambda_0^2 (m_1 + m_2) N};$$

$$m_r = \frac{m_{\text{Al}} m_{\text{O}}}{(m_{\text{Al}} + m_{\text{O}}) N_A},$$

where c is the velocity of light; m_1 and m_2 are atomic weights of the ions; λ_0 is the wavelength of natural vibrations; N_A is the Avogadro number; m_r is the reduced mass.

First, the reduced mass was calculated; next, the wavelengths of natural vibrations λ , natural vibration frequencies ω_0 , and the elastic bond coefficient at $\omega \ll \omega_0$:

$$\lambda = \frac{1}{\nu};$$

$$\omega = \frac{4\pi c}{\lambda};$$

$$k = \omega_0^2 m_r.$$

It should be noted that usually ω_0 and k cannot be calculated and are found experimentally.

In a range remote from resonance ($\omega \ll \omega_0$), an approximated formula can be used for polarizability:

$$\alpha_n = \frac{r_1 + r_2}{n - 1},$$

where r_1 and r_2 are the radii of the ions; n is a constant within the range of 7–11.

In some cases it is possible, for complex molecules, to consider single bonds and not the molecule in general, which is corroborated by the emergence of a respective absorption band in the IR spectrum [7].

Since oxygen ions are uniformly distributed among the vibration types, each type of stretching vibrations correlates with 1/6 oxygen ions for Al_2O_3 and 1/4 for SiO_2 . Consequently, the contribution of stretching vibrations to dielectric permeability can be calculated based on the formulas

$$\varepsilon(\text{Al}_2\text{O}_3) = \frac{n_0}{6} \left(\frac{\alpha_1 + \alpha_2 + \dots + \alpha_n}{\varepsilon_0} \right);$$

$$\varepsilon(\text{SiO}_2) = \frac{n_0}{4} \left(\frac{\alpha_1 + \alpha_2 + \dots + \alpha_n}{\varepsilon_0} \right).$$

The resultant ε at the exit from the IR range of the spectrum can be determined from the formula

$$\varepsilon_{\infty} = \varepsilon_{\text{exp}} + \varepsilon(\text{Al}_2\text{O}_3) + \varepsilon(\text{SiO}_2).$$

The values calculated on the basis of these formulas are given in Table 3.

Thus, taking into account elastic ionic polarization, the values $\varepsilon_{\infty} = 5.23$ for ultraporcelain UF-46 and $\varepsilon_{\infty} = 6.146$ for electroporcelain M-23 are between the experimental data obtained by petrography methods in the visible spectrum range for frequency 1 MHz, which satisfactorily agrees with the nature of dielectric processes in high-alumina ceramics.

A theoretical polarization model can be used to calculate relaxation polarization for weakly bonded ions.

Calculation of the contribution of polarization of the i th impurity to dielectric permeability $\Delta\varepsilon_i$ in the technical frequency range was performed using the formula

$$\Delta\varepsilon_i = \varepsilon_{\infty} + \frac{n_i \alpha'_i}{\varepsilon_0},$$

where ε_{∞} are theoretical results obtained in the optical range of the IR spectrum; n_i is the concentration of impurity ions; α'_i is the real part of static polarizability; ε_0 is the electric constant.

The range of relaxation of weakly bonded ions is equal to the interatomic distance in porcelain.

The contribution of weakly bonded sodium ions to permeability in porcelain M-23 and UF-46 was determined. To calculate the actual part of statistic polarizability, the following formula was used:

$$\alpha'_i = \frac{q^2}{m \omega_0^2}.$$

Estimated values of dielectric permeability in the range from IR to 1 MHz amounted to 5.35 for ultraporcelain UF-46 and 6.35 for electroporcelain M-23. Calculations were performed using the classical Debye relaxator with two equilibrium positions.

Theoretical studies show that the vibration model of relaxation polarization proposed in [10] gives sufficiently good quantitative convergence in describing dielectric permeability spectra in the technical frequency range.

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